ELECTROCHEMICAL PERFORMANCE TESTING

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OVERVIEW

Timeline

- Facility established: 1976
- End: Open – this is an on-going activity to test/validate/document battery technology as technologies change and mature

Budget

- DOE Funding FY17: $1.8 M
- FY16: $1.8 M
- FY15: $2.0 M

Barriers

- Performance (power and energy densities)
- Cycle life (1,000-450,000 depending on application)
- Calendar life (15 y)
- Low-temperature performance

Collaborations

- US battery developers
- Idaho National Laboratory, Sandia National Laboratories
- CATARC (China)
- Purdue Univ., Battery Innovation Center

RELEVANCE

Objective

- To provide DOE and the USABC an independent assessment of contract deliverables and to benchmark battery technology not developed under DOE/USABC funding
- To provide DOE and the USABC a validation of test methods/protocols
- To develop methods to project battery life and to use these methods on test data

Approach

- Apply standard, USABC testing methods in a systematic way to characterize battery-development contract and benchmarking deliverables
- Characterize cells, modules and packs in terms of:
  - Initial performance
  - Low temperature performance/Cold cranking
  - Cycle life
  - Calendar life
- Compare test results to DOE/USABC goals
- Adapt the test facility hardware and software
  - to accommodate programmatic need
  - to accommodate the unique needs of a given technology and/or deliverable

PROGRAM MILESTONES

Milestone	Date	Status
Submit quarterly reports to DOE and USABC	12/31/16	Complete
Submit quarterly reports to DOE and USABC	3/31/17	Complete
Submit quarterly reports to DOE and USABC	6/30/17	On track
Submit quarterly reports to DOE and USABC	9/30/17	

TECHNICAL ACCOMPLISHMENTS: PROGRESS AND RESULTS – TESTING CONTRACT DELIVERABLES

- Test deliverables are mostly cell-oriented and include developments in
  - Lithium-ion battery chemistry (graphite anodes)
  - Silicon anodes
  - Battery recycling
  - Ultra capacitors
  - Lithium metal anodes
  - Separators
  - Advanced cell chemistries (beyond Li-ion)
- Deliverables are characterized in terms of initial capacity, resistance, energy and power. They are then evaluated in terms of cycle and calendar life for the given application
- Results are used to show progress toward meeting DOE/USABC initial commercialization goals

PROGRESS AND RESULTS – TESTING CONTRACT DELIVERABLES

Developer	Sponsor	Level	Quantity	Rated Capacity, Ah	Application	Status
JCI	USABC	Cell	9	27	PHEV-20	complete
	DOE FOA	Cell	18	15	PHEV-20	complete
	DOE FOA	Cell	4	15	PHEV-20	complete
	DOE FOA	Cell	23	3	PHEV-20	complete
Leyden	USABC	Cell	30	2.2	12-V S/S	complete
Maxwell	USABC	Cell	6	0.357	12-V S/S	complete
	USABC	Module	15	40	12-V S/S	on-going
	USABC	Cell	20	0.357	12-V S/S	on-going
24-M	USABC	Cell	6	0.79	EV	on-going
	USABC	Cell	18	6	EV	on-going
	DOE FOA	Cell	10	4.3	EV	on-going
	DOE FOA	Cell	4	105	EV	on-going
Xerion	USABC	Cell	21	0.92	PHEV-20	on-going
3M	2013 ABR	Cell	12	2.88	EV	complete
Navitas	DOE FOA	Cell	24	14	EV	on-going
	DOE FOA	Cell	13	2/4	EV	complete
Tiax	2013 ABR	Cell	13	1.8	EV	complete
	2013 ABR	Cell	13	2.1	EV	on-going
ANL (J. Zhang)	DOE FOA	Cell	15	0.16	EV/PHEV	complete
Seeo	DOE	Cell	6	11	EV	complete
LGChem	DOE	Cell	10	25.9	PHEV-40	on-going
XALT	DOE FOA	Cell	24	95	EV	on-going
Wildcat	DOE	Cell	20	1.7	EV	complete
WPI	USABC	Cell	50	2	Recycling/PHEV-20	on-going
	USABC	Cell	30	25	Recycling/PHEV-20	on-going
SiNode	USABC	Half cell	9	0.00236	EV	on-going
	USABC	Cell	8	0.00156	EV	on-going
	USABC	Cell	20	1	EV	on-going
Microcure	DOE	Cell	6	2.2	EV	on-going
Farasis	USABC	Cell	18	2	Recycling/PHEV-20	on-going
	USABC	Cell	18	2	Recycling/PHEV-20	on-going
	USABC	Cell	30	25	Recycling/PHEV-20	on-going
Daikin	DOE	Cell	9	1	EV/PHEV	on-going

- Test deliverables come from many developers
- Deliverables are tested for various automotive applications

PROGRESS AND RESULTS – COLLABORATIVE US/CHINA FAST CHARGE COMPARISON

- There are parallel testing efforts, such as those in the US and China
- These efforts may be better leveraged through international collaboration
- With further vehicle electrification, customers would desire battery charging to take the same amount of time as refueling an ICE does at a service station. This does not have to be a full charge
- The Chinese Fast Charge Test consists of full cycles from empty to full including CV to manufacturer recommended taper at 25^{o}C.
- For comparison, complete fast charge cycles from empty to full were applied to an additional group of cells at 30^{o}C, using USABC metrics for RPTs.
- Future collaborative work will compare these degradations to those defined in the USABC rev 2 and rev 3 EV manuals. Rather than full cycles, the USABC EV manual definitions are:
  - Fast charge from 60% DOD to 20% DOD at increasing rates (rev 2)
  - Fast charge from 80% DOD at 3.2C for 15 minutes. CV as necessary (rev 3)

CONDUCT SIDE-BY-SIDE EXPERIMENTS

- A test plan based on an EV application was written and agreed to
- Commercially-available batteries based on $LiFePO_4$ and carbon were procured. The batteries were distributed to ANL and CATARC (China)

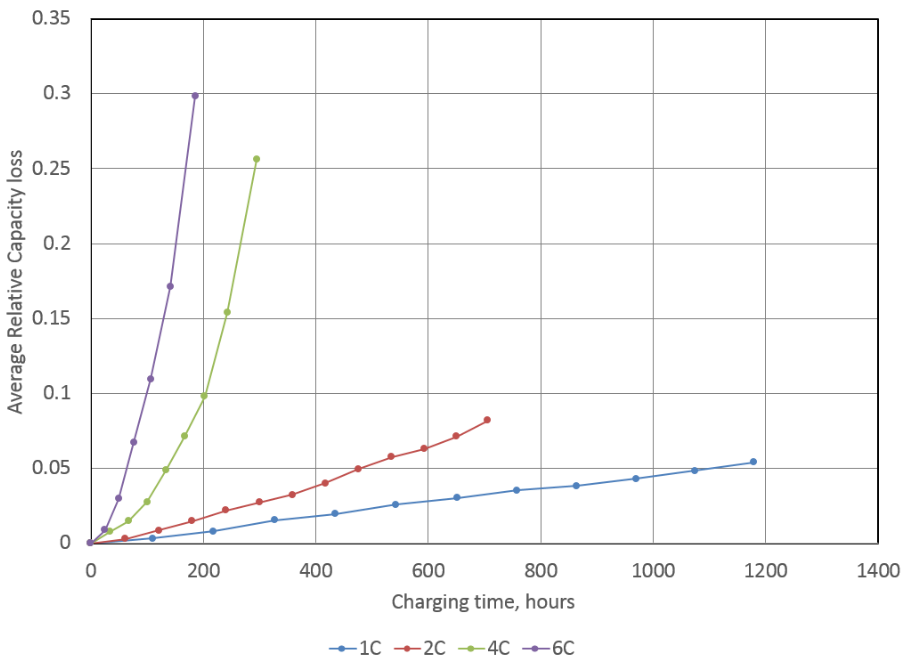
Test Name	Protocol	Charge Rates	Temperature (°C)	RPT capacity rate	Power pulse	Pulse DOD
Fast Charge - US	Full cycles from empty to full	1, 2, 4 and 6-C	30	C/3	20A, 30s	Every 10%
Fast Charge - China	Full cycles from empty to full	1, 2, 4 and 6-C	25	C/1	45A, 5s	50%

  - All tests used full capacity cycles at 1-C, 2-C, 4-C and 6-C charging rates
  - Discharge was always at 1-C rate for aging
  - Thirty minute rest periods between steps
  - Three cells per condition
  - USABC Reference Performance Test consisted of 1 C/3 capacity cycle and 30 second peak power pulse test at 10% DOD increments. The cells are characterized using these performance tests every 100 cycles at 30°C
  - China Reference Performance Test consists of 1 C/1 capacity cycle and 5 second discharge pulse after discharging at C/1 for 1800 seconds. The performance of the cells were characterized using these performance tests every 100 cycles at 25°C

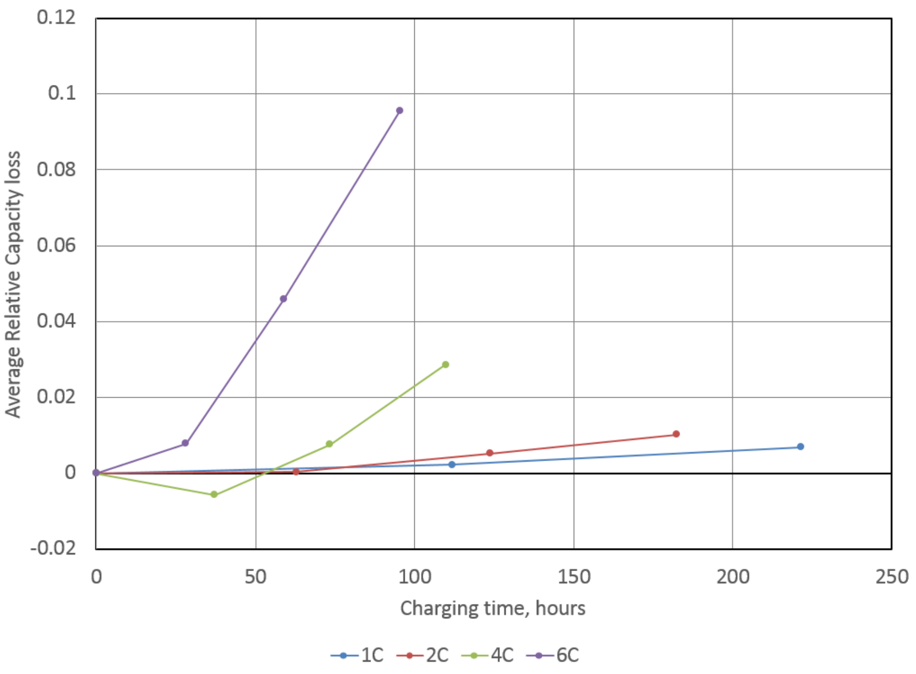
CAPACITY FADE OVER CYCLE LIFE

- Faster charge rates caused faster capacity fade
- Rates above 2-C show non-linear fading

US protocol (C/3 capacity)

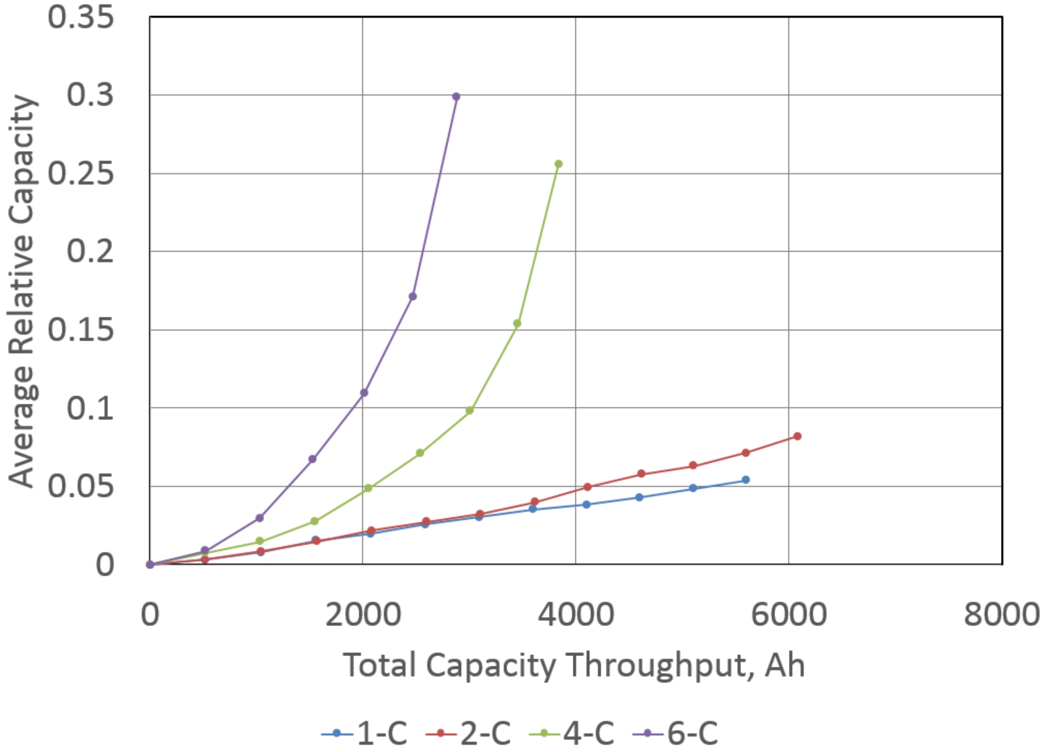


China protocol (C/1 capacity)



CAPACITY FADE OVER THROUGHPUT

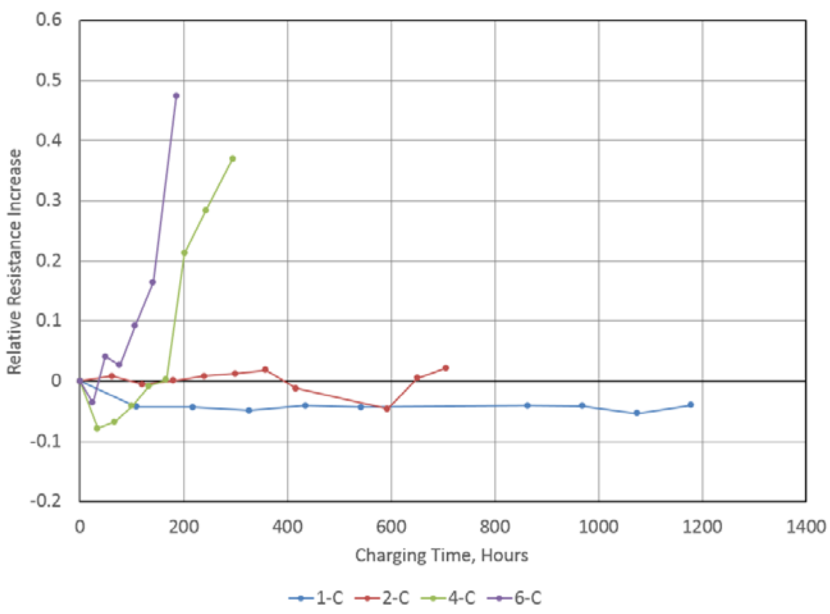
- Using total accumulated Ah instead of time, 1-C and 2-C are similar up to 3000Ah of total throughput
- 4-C and 6-C rates are similar for the first 500Ah throughput
- Faster charging rates degrade more over capacity throughput



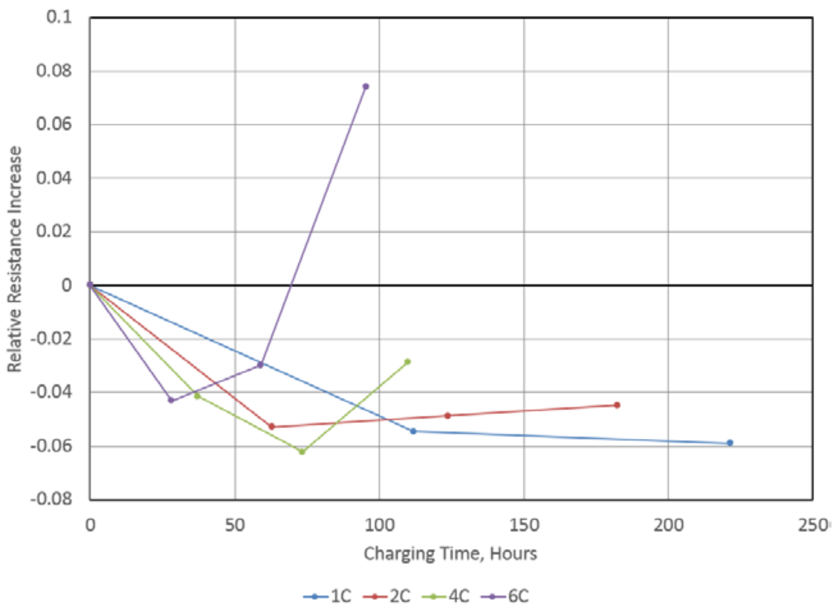
RESISTANCE INCREASE AT 50% DOD

- Chinese protocol only tested at ~50% DOD, best area for comparison
- US test shows resistance decrease for 1-C rate cells and negligible change at 2-C
- Other rates show resistance increase

US protocol (20A, 30sec pulse)

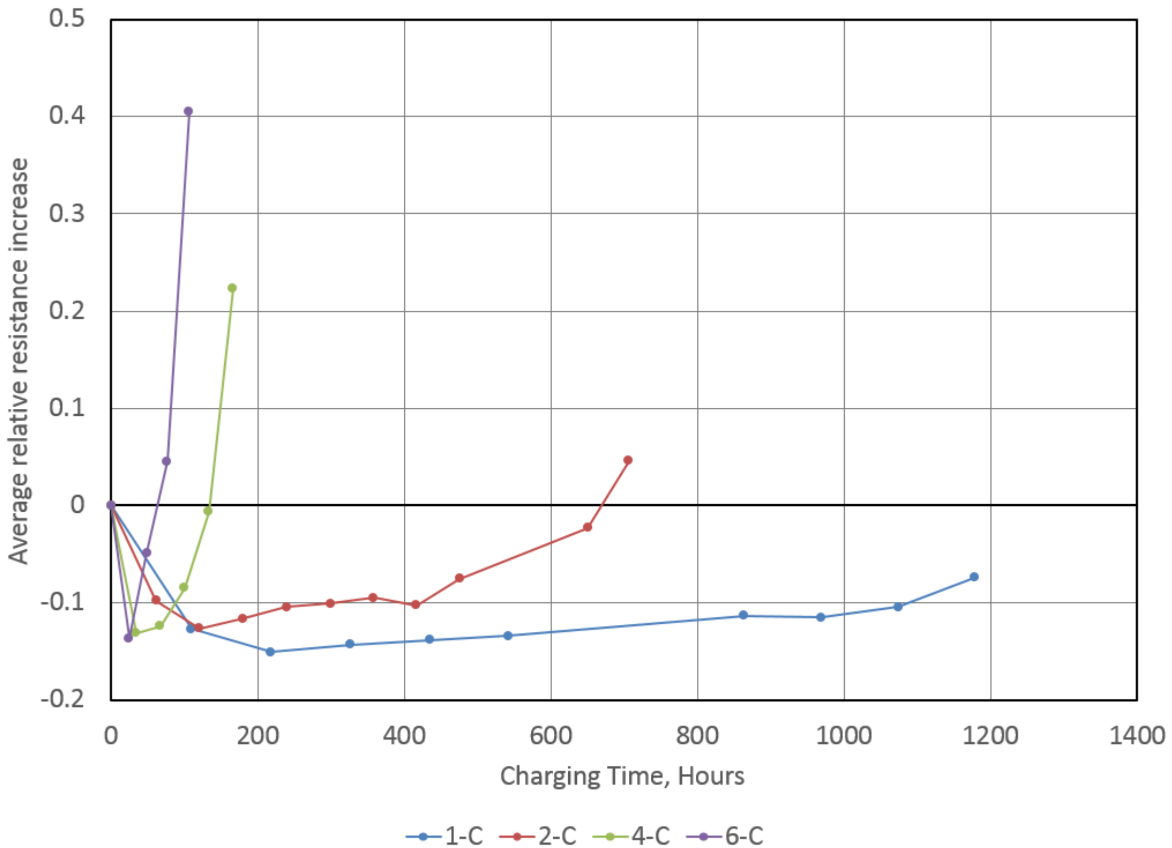


China protocol (45A, 5sec pulse)



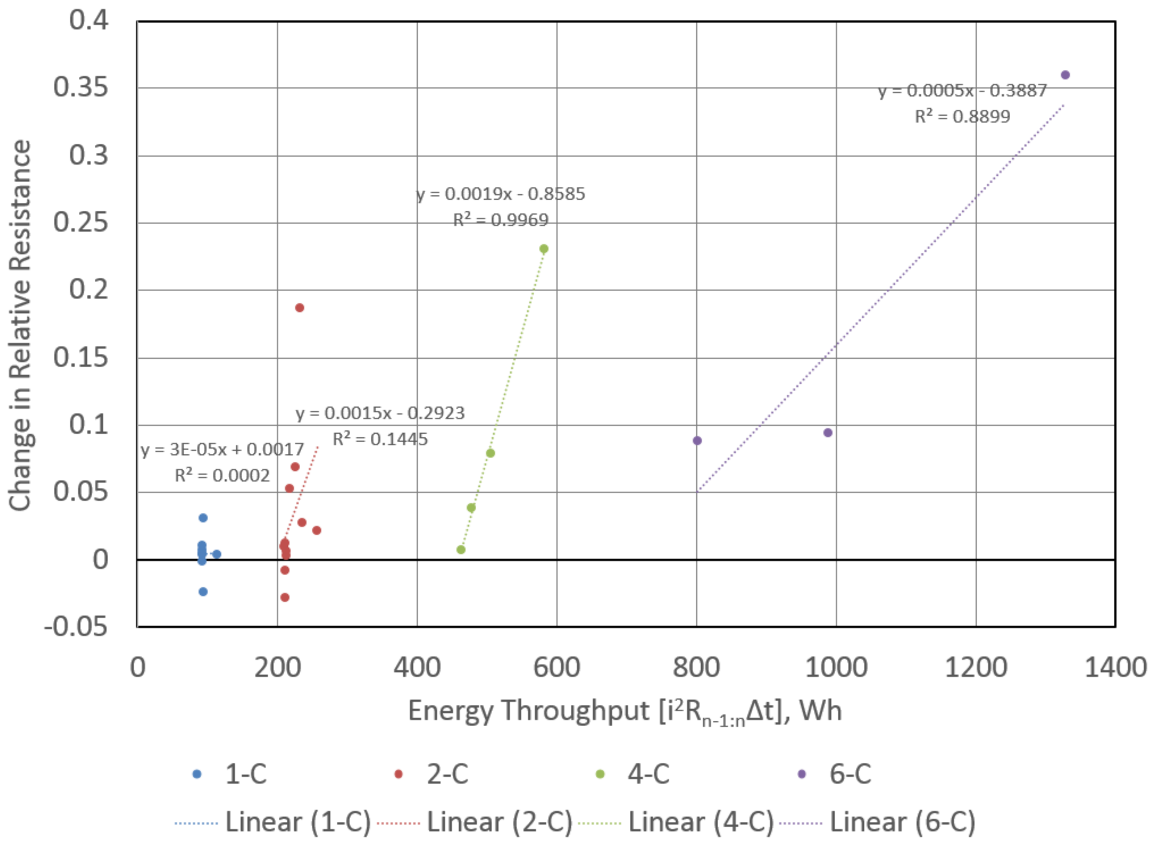
RESISTANCE AT 80% DOD

- Resistance drops more significantly at beginning of life for 80% DOD then for 50% DOD
- For rates above 2-C, rise is faster than 50% DOD pulses



RESISTANCE GROWTH VS ENERGY THROUGHPUT

- Rates 2-C and below do not appear to have a strong correlation between heat generation and resistance growth
- Fast rates appear to have a relationship between heating and resistance growth



CC AND CV CHARGE CAPACITY DISTRIBUTION

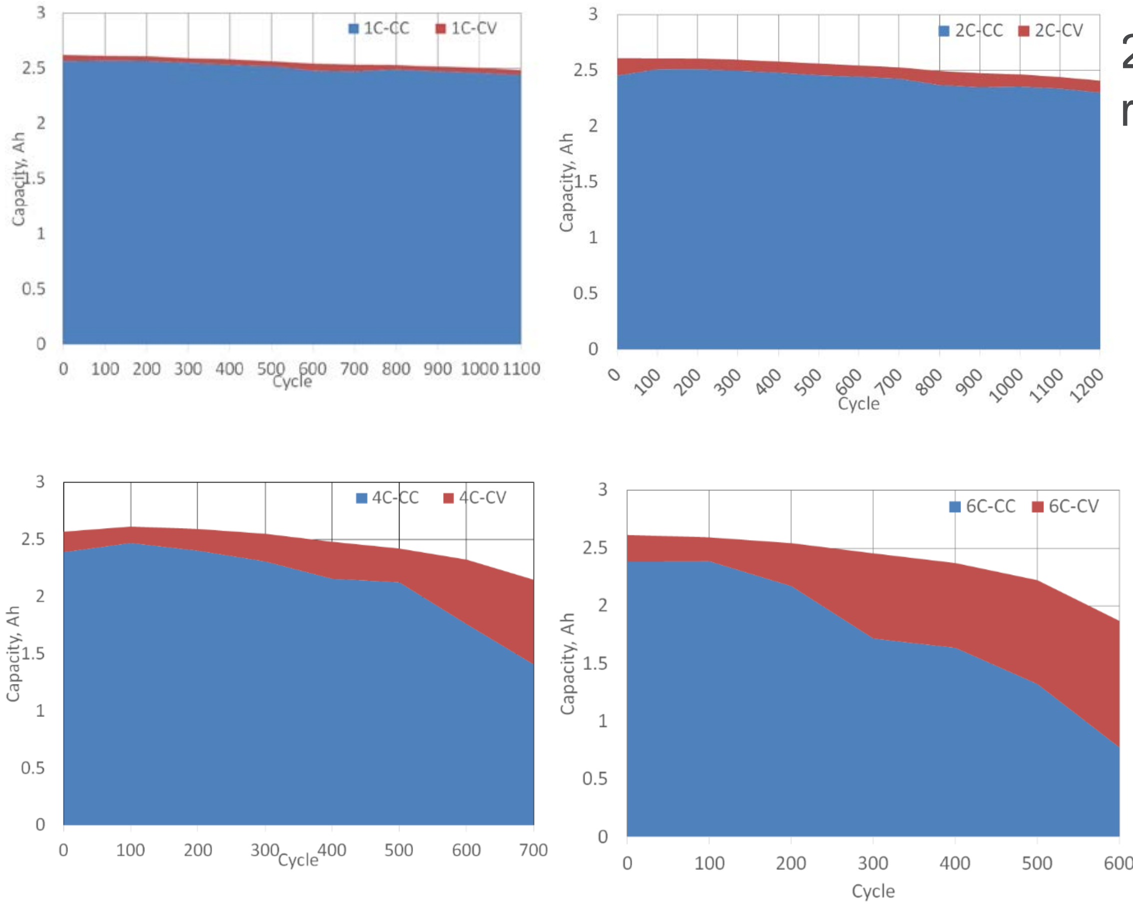
- For rates above 2-C, shift from most capacity in constant current step to more capacity in constant voltage step

1-C rate

2-C rate

4-C rate

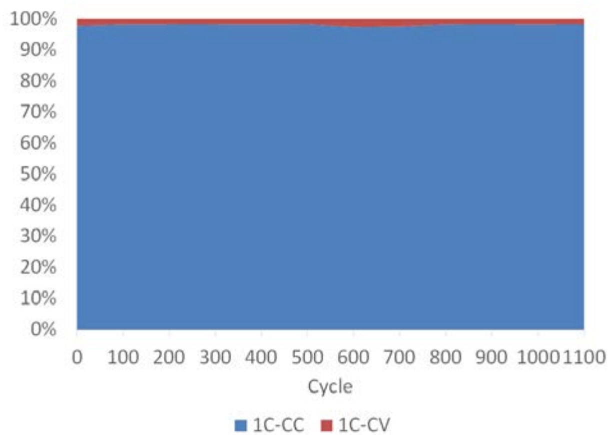
6-C rate



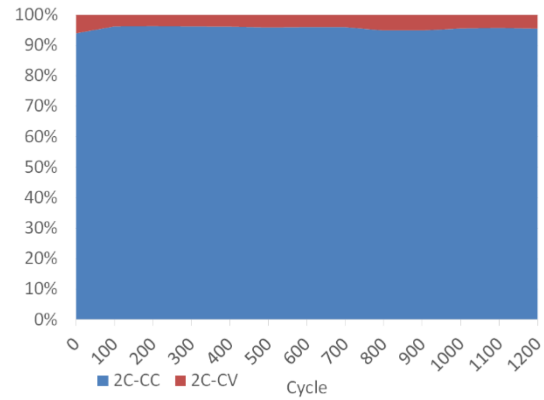
DISTRIBUTION OF CAPACITY BETWEEN CC AND CV

- Most capacity returned during CC step through life at rates of 2-C and below
- By end of life, less than 50% of capacity returned during CC step at 6-C rate compared with 10% at beginning of life

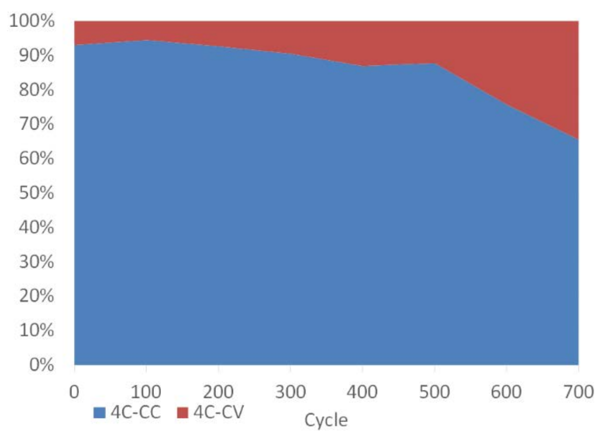
1-C rate



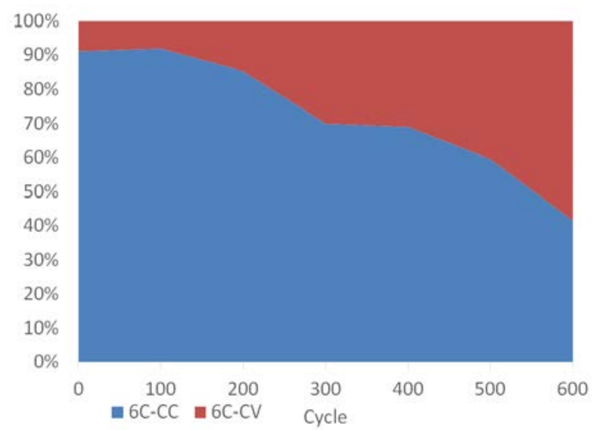
2-C rate



4-C rate



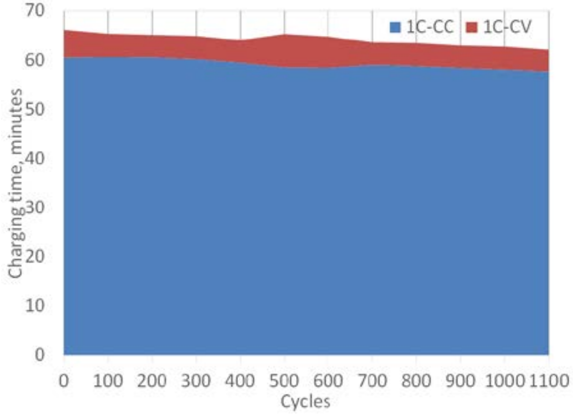
6-C rate



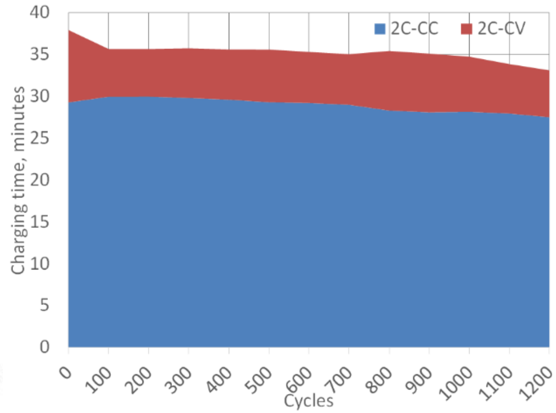
CC AND CV TIME DISTRIBUTION

- Despite capacity fade, charging rates above 2-C require more and more time to fully charge
- By end of life, most of charging time in CV mode above 2-C rate
- After 600 cycles, 4-C charge rate faster than 6-C even though higher capacity

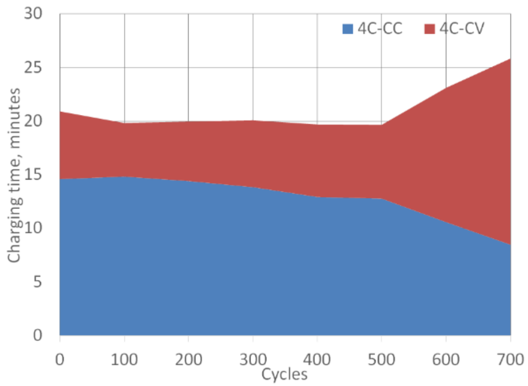
1-C rate



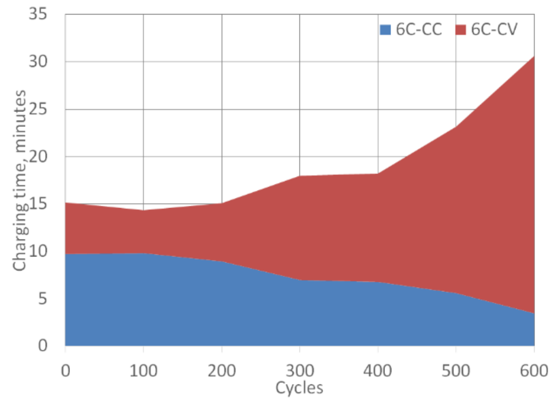
2-C rate



4-C rate



6-C rate

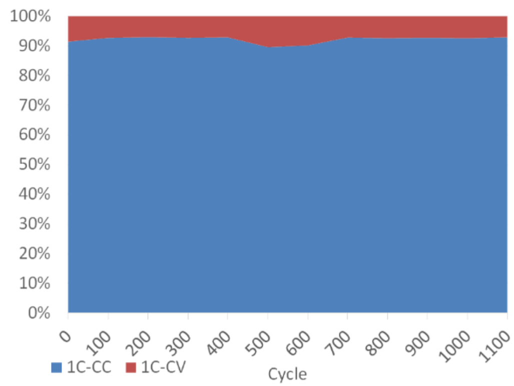


6C charging time goes from 15 minutes to 30 minutes after 600 cycles despite 30% capacity loss

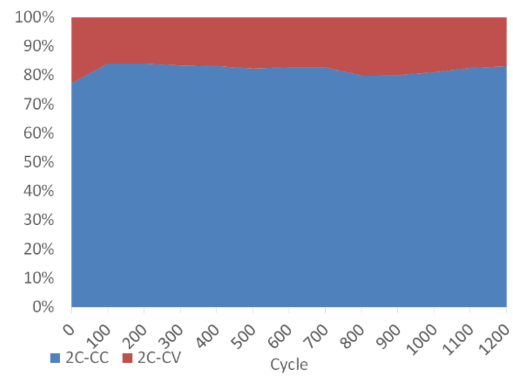
PERCENTAGE OF TIME IN CC AND CV MODES

- At beginning of life, 6-C rate reaches Vmax in 64% of the total charge time
- By end of life, only 11% of total charge time to reach Vmax at 6-C rate
- Higher resistance causes longer CV and overall charging time at 4-C and above
- Eventually it takes more time to put less energy into the cell at high rates

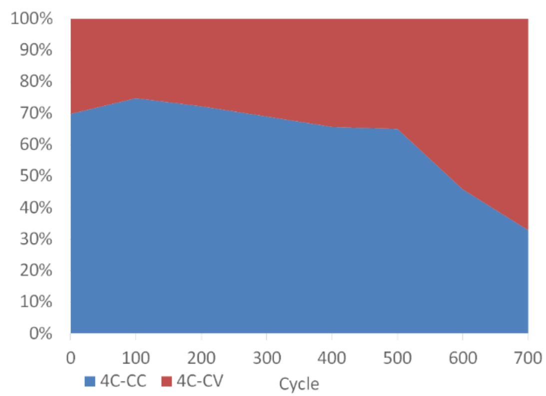
1-C rate



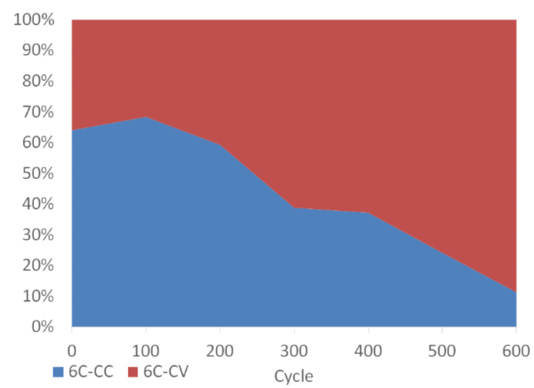
2-C rate



4-C rate



6-C rate



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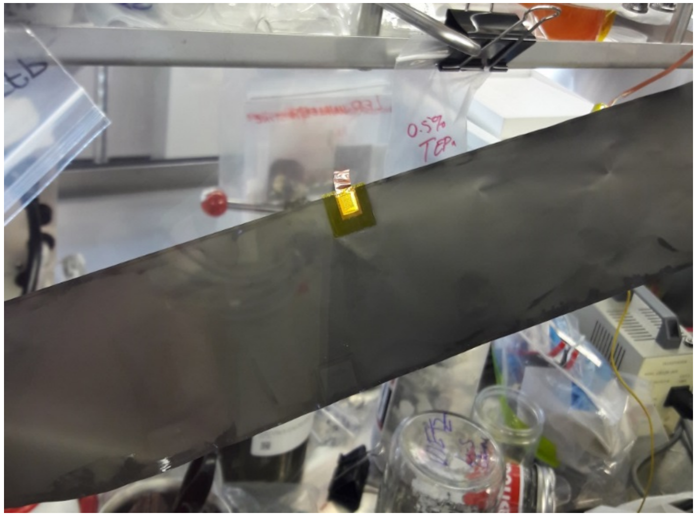
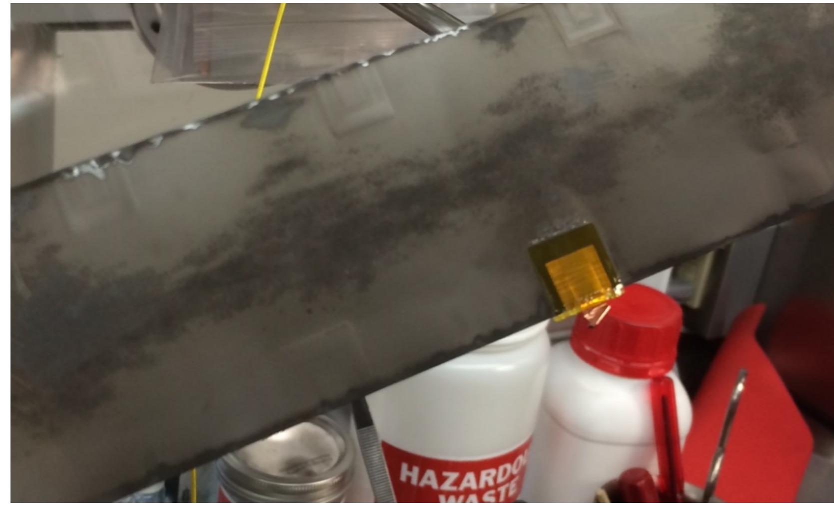
POST TEST OBSERVATIONS - ANODE

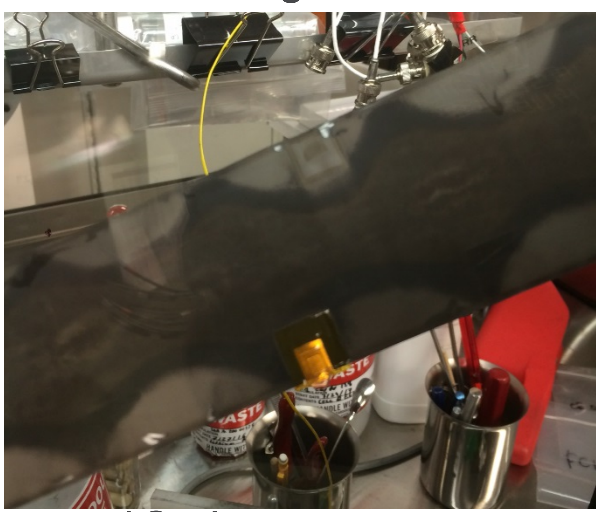
- Initial tear down shows signs of material degradation at higher rates



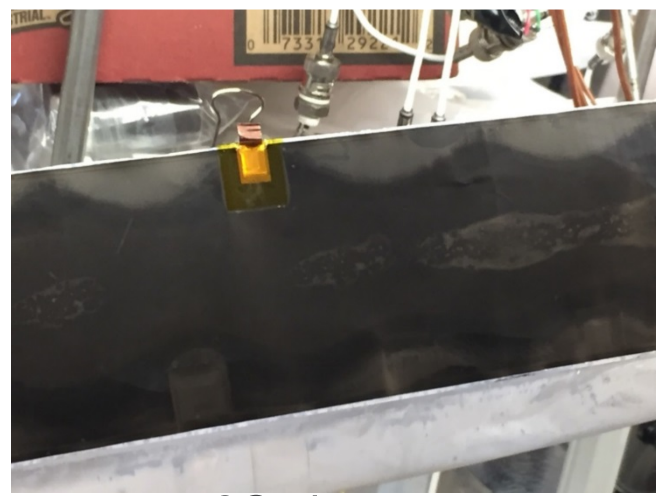
1C charge rate



2C charge rate



4C charge rate

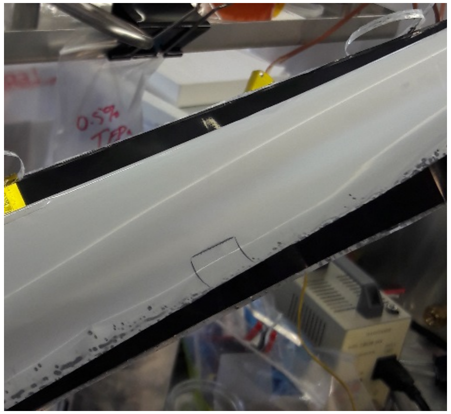


6C charge rate

POST TEST OBSERVATIONS - ANODE

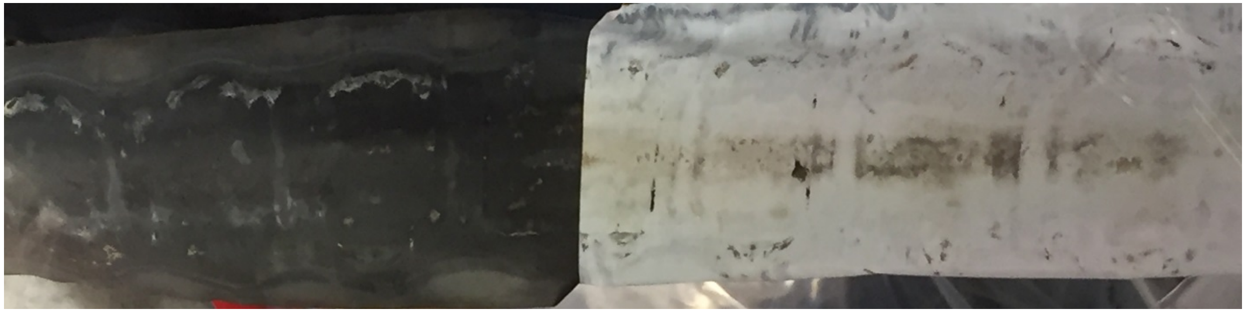
- No staining seen on separator at 1C rate
- The amount of staining on separator seems to increase with charge rate

1-C rate



6-C rate

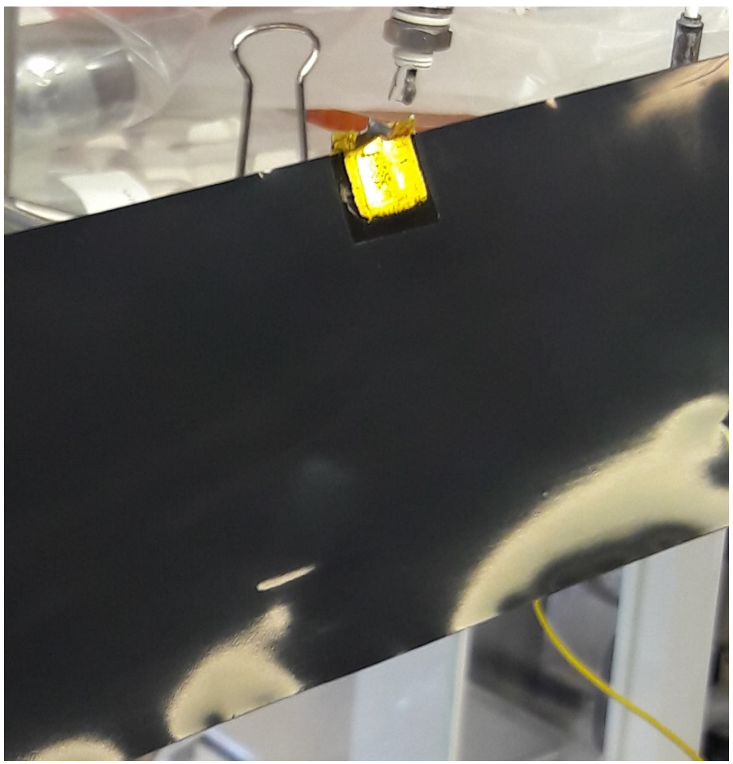
6-C rate



POST TEST OBSERVATIONS - CATHODE

- No visible difference between cathodes at each rate

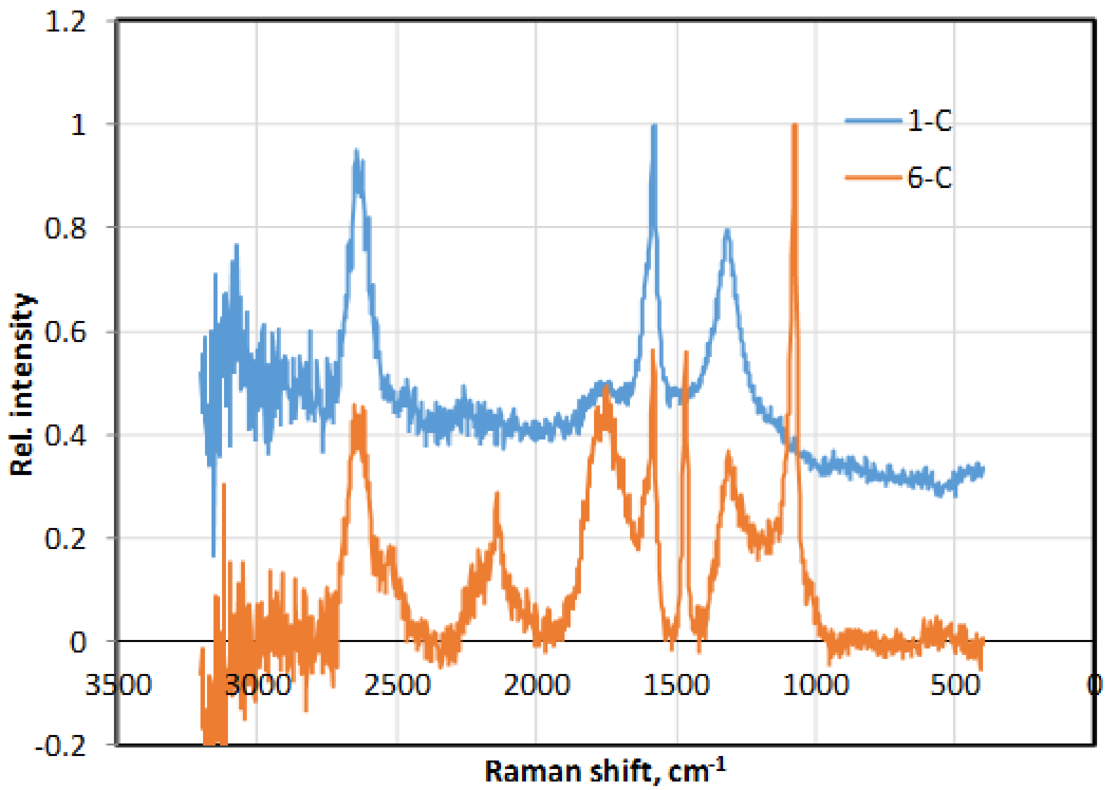
1-C rate



4-C rate

CHANGES SEEN IN RAMAN SPECTRA

- Indications of electrolyte reactions at high rates
- Observed bands due to C=O and C-O



SUMMARY AND FUTURE WORK

- Summary
  - Hardware deliverables from many sources have been tested at Argonne and continue to be evaluated for a variety of vehicle applications
  - This testing directly supports DOE and USABC battery development efforts
  - The US/China EV testing has shown
    - Faster charge rates accelerate capacity fade and resistance rise
    - Charging times can increase despite aging mechanisms
- Future Work
  - Continue to support the DOE and USABC battery development efforts by performing unbiased evaluations of contract deliverables, using standardized test protocols
  - Compare results of full fast charge between ANL and CATARC in China
  - Continue collaboration with CATARC using USABC partial charge definitions on $LiFePO_4$-based cells

Any proposed future work is subject to change based on funding levels

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THANK YOU.

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